PATENT SPECIFICATION

982,759

DRAWINGS ATTACHED

982,759

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Int. Cl.:—C 01 b

COMPLETE SPECIFICATION

Carbon Products with a Predetermined Distribution of Pores

We, UNITED KINGDOM ATOMIC ENERGY AUTHORITY, London; a British Authority, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to methods of making carbon articles from carbonaceous particles and aims to provide a process step in such methods which will enable the size distribution of the open pores of the carbon article to be predictable to some extent.

The applicant has studied a large number of mixtures of graphite powder and/or coke powder and/or carbon black which have served as the raw materials for the production of graphite. A new process step has been discovered by the applicant, which is the subject of the present invention, which makes it possible to obtain graphitised products having a relatively narrow and to some extent a predetermined distribution of pores by using carbonaceous raw materials which have a well determined grain size distribution closely related to the desired distribution of pores in the finished final product.

More particularly, the applicant has established that it is a certain grain size distribution of the fine particles used which essentially determines the pore distribution of the final product whilst the grain size distribution of the large particles used has a relatively small effect on the size of these pores.

The industrial products made by the procedure in accordance with the present invention make it possible to achieve considerable technical progress in their application for exceptionally impermeable materials, in particular for nuclear reactors.

According to the present invention there is provided a method of making a carbon article having at least 80% of the total volume of the open pores of the finished article formed of pores having a predetermined range of diameters between dimensions a and b as herein defined, which resides in forming a grist composed of sized carbonaceous particles according to the following conditions:—

(i) 90% of the particles by weight having a diameter greater than a

(ii) from 50-70% by weight of particles having a diameter greater than b, and

(iii) at least 15% of the particles having a diameter between b and $20b$, where a is any dimension between 0.03 and 1,500 microns and b is between $3a$ and $10a$, and

in subjecting the grist thus obtained to a carbonizing process. Preferably the dimension b is between $5a$ and $7a$.

A grain size mixture as defined above is easily obtained by the systematic use, already known, of techniques of grinding, sieving, air selectors, etc. and of mixing operations. It is known, for example, that particles of diameter greater than 35 microns can be sorted with the aid of sieves, that those with a diameter of between 35 and 1 micron can be sorted by apparatus known under the name of air elutriators and that the range of particles smaller than 1 micron, which constitutes carbon black, can also be obtained in accordance with a predetermined grain size distribution substantially without difficulty.

The determination of the distribution of the volume of pores of the product according to the diameter—which is necessary to check that the finished final product is in agreement with the data for the distribution of pore diameters which has been laid down in advance—is carried out at pressures up to 500 kg/cm² by means of a mercury porosimeter, which makes it possible to measure the percentage of pores accessible to mercury up to a maximum pressure of 1,000 kg/cm².

The raw product which has been obtained according to the procedure described above, may be subjected to baking under pressure, pneumatic or other, by any technique already

known.

The baked product obtained according to the procedure described above may be graphitised.

The baked or graphitised product may be impregnated according to any known technique by means of a substance, e.g., pitch, thermo setting or thermo plastic materials. This impregnation is followed by baking and possibly by graphitisation. The cycle consisting of impregnation followed by baking and possibly by graphitisation may be repeated several times.

The applicant has found that baking under pressure, and impregnation, brings about an advantageous and considerable decrease in the total porosity of the product, and/or a very considerable diminution in the proportion of fine pores, which may in fact disappear almost entirely.

Examples 1 to 5 below are intended to explain various aspects of the invention and to illustrate how the invention can be put into practice. Example 1A does not form part of the invention, but is merely illustrative of a departure from the invention.

All the examples 1-5 were carried out with a grist composed of at least one of five raw materials, A, B, C, D and E whose grain size distribution are represented graphically in the accompanying Figure 1 and numerically in Table 1.

TABLE 1

The approx. diameter 'd' of particles in microns	Percentages by weight of particles of diameter greater than 'd'				
	A	B	C	D	E
200	3%				
80		5%			
75	50%		0%		
60			16%		
30		50%			
20	85%		29%		
10		73%	43%	1%	
5.5				3%	
3.5				25%	
3			70%		
2	99%	93%			
1			91%		
0.5				93%	1%
0.3					50%
0.2					87%
0.1					99%

Figure 1 shows a series of curves A—E of the respective particle size distribution A—E in which the percentages by weight are plotted as ordinates for particles of a diameter exceeding the value d (microns) plotted as abscissa on a logarithmic scale. The percentage weight is related to the total weight of the particles used.

Of the other accompanying drawings, Figures 2-6 show a series of curves on an abscissa *d* in microns-pore diameter or grain diameter and of which one curve is the grain size distribution on the same ordinates as Figure 1 and designated G1, G2, G3 etc. to correspond with the appropriate example. G1′ corresponds with example 1A. Further curves, designated P1, P2, P3 etc. for the same reason, are plotted on the same abscissa with the ordinate scaled in porosity P. Pore volume, expressed as a percentage of the bulk volume, accessible through pore size indicated on abscissa.

Also Figures 2, 3, 5 and 6 have differentials of curves P1, P2, P4, P5 and P6, designated R1, R′ and R3 with the ratio $R=\frac{\Delta P}{\Delta \log . d}$ expressed as percentage, as ordinate and *d* as abscissa.

The shaded surface between curve R and the abscissa gives the porous volume between two given sizes dimensions of pores. R is easily drawn on the basis of curve P. R1 relates to example 1, R3 relates to example 3 etc.

The pairs of vertical dotted lines α and β on the graphs define the limits of the ranges laid down by the first two conditions (i) and (ii) in the consistory clause as follows: the dotted line α has an abscissa equal to *a* and ordinates extending over the range 90%-100% (condition (i)) and the dotted line β has an abscissa equal to *b* and ordinates extending over the range 60%-70% (condition (ii)).

The point C on each graph is defined as follows:—

C has an abscissa equal to $20b$

C has an ordinate equal to a value which is 15% less than the ordinate of the curve G corresponding to the abscissa b

The position of the point C defines the third condition (iii) of the consistory clause.

For examples 1-4 the dimension a is fixed at 0.2 microns and the dimension b is thus between 0.6 to 2 microns from which we select the dimension 1 micron.

A large number of curves G, and among these the curves G1, G2, G3 and G4 corresponding to examples 1 to 4, are able to satisfy the 3 joint conditions (i), (ii) and (iii) given above. The mixtures used are as shown in Table 2.

TABLE 2

Examples	Percentage By Weight Used Of The Various Components				
	A	B	C	D	E
Example 1	44, 5%		22, 5%		33%
Example 1A	67%				33%
Example 2			67%		33%
Example 3	22, 5%		44, 5%		33%
Example 4	44, 5%			22, 5%	33%
Example 5		100%			

Table 1 and the curves in Figure 1 supplement the values given in Table 2.

EXAMPLE 1.

This example which is more particularly illustrated by the curves G1, P1 and R1 of Figure 2 shows a grain size distribution curve G1 in accordance with the conditions (i), (ii) and (iii) above and shows the predetermined result, i.e. a pore volume distribution of size between 0.2 and 1 micron of the order of 80% according to curves P1 and R1.

EXAMPLE 1A. (For comparison with Example 1).

This example is illustrated in curves G′, P′ and R′ in Figure 3.

In this example the values of a and b are taken as the same as those in Example 1 but a grain size curve G′ passes *above* the point C′ which is contrary to the condition (iii) above.

In consequence one finds by means of curves P′, R′ only 50% of the total pore volume consists of pores between 0.2 and 1 micron, that is definitely less than 80%.

EXAMPLE 2.

This example is illustrated by curves G2 and P2 in Figure 4. The curve G2 satisfies the three conditions (i), (ii) and (iii) above and one finds with the aid of curve P2 that the pore volume corresponding to a pore diameter between 0.2 and 1 micron is about 91%.

EXAMPLE 3.

This example is illustrated by curves G3, P3 and R3 in Figure 5.

The grain size distribution expressed by curve G3 satisfies the three points 1, 2 and 3 defined above. As a predetermined result, the pore distribution which is measured by the curves P3 and R3 is about 84% of the total pore volume of diameters between 0.2 and 1 micron.

EXAMPLE 4.

This example, illustrated by curves G4, P4 and R4 in Figure 6, shows a grain size distribution G4 in accordance with the procedure under the invention and the pore volume distribution according to curves P4 and R4 of the order of 90%.

EXAMPLE 5.

This concerns a region of pore size which is different from that in examples 1 to 4. In example 5 we take $a'=1.6$ microns and $b'=16$ microns. This example is more particularly illustrated by curves G5 and P5 in Figure 4. We see that G5 satisfies the conditions of the procedure under the invention.

P5 shows likewise a distribution of pores between the given limits (1.6-16 microns) of about 93% of the total.

Examples 1 to 4 above illustrate, among other things, the unexpected fact that, in accordance with the procedure, one can obtain final carbonised products which have pore distributions very similar to one another although using several mixtures of different raw materials, each having a particular grain size distribution which is perceptively different from that of the other raw materials. This shows in particular, the flexibility of operation and ease of exploitation that can be obtained by means of the present procedure. The choice of one or another raw material is often dictated, for example, by considerations of cost.

Industrial application of these products is also the object of this invention. These applications include in particular.

A. The use as a material for further impregnation, in order to make products which can be used, after such impregnation and any subsequent treatments, as impermeable barriers to gas or molten metals. Such impermeability is particularly useful in nuclear reactors. These impregnated products can also be used for electrodes operating in a fused or aqueous medium or as a lining material for crucibles, or cells for electrothermal operations.

B. The use as a porous material of a well defined type, e.g. in processes which involve diffusion or infiltration in the gaseous, liquid or molten phases including use as a material of construction for the gaseous diffusion of uranium hexafluoride, or as material for filter plates or filter crucibles.

WHAT WE CLAIM IS:—

1. A method of making a carbon article having at least 80% of the total volume of the open pores of the finished article formed of pores having a predetermined range of diameters between dimensions a and b as herein defined, which resides in forming a grist composed of sized carbonaceous particles according to the following proportions:—

   90% of the particles by weight having a diameter greater than a, from 50-70% by weight having a diameter greater than b, and about 15% by weight having a diameter between b and $20b$ where a is any dimension between 0.03 and 1,500 microns and b is between $3a$ and $10a$

and subjecting the grist to a forming process.

2. A method of making an article as claimed in claim 1 including a graphitising process.

3. A method as claimed in claims 1 or 2 in which the dimension b is between $5a$ and $7a$.

4. As a step in the process for making from carbonaceous particles an artefact whose open pore size distribution is predetermined beforehand to the extent that at least 80% of the total open pore volume of the finished article is composed of pores whose diameters fall within range a and b as herein defined, the preparation of a grist of sized carbonaceous particles according to claim 1.

5. A product produced by a process which includes the process step as claimed in any of claims 1 to 4.

M. T. HUNT,
Chartered Patent Agent.
Agent for the Applicant.

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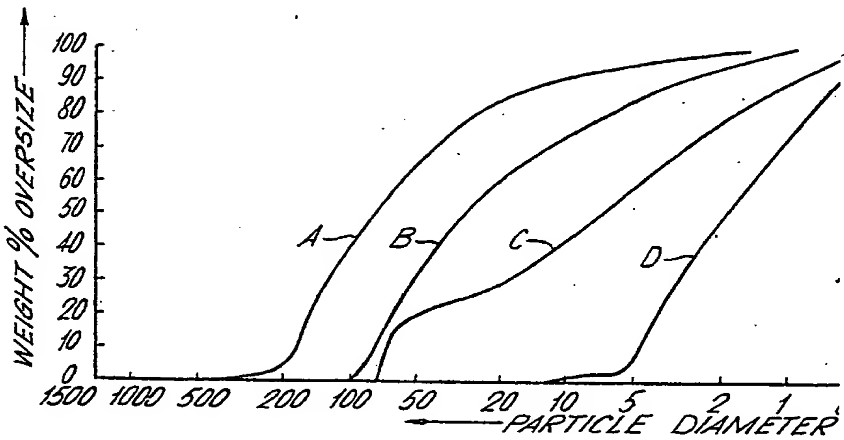
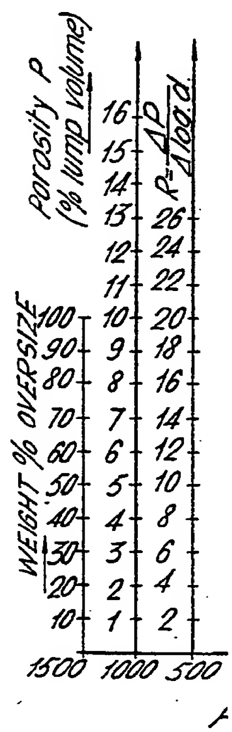
FIG.1.


WEIGHT % OVERSIZE
100
90
80
70
60
50
40
30
20
10
0
A
B
C
D
1500 1000 500 200 100 50 20 10 5 2 1
PARTICLE DIAMETER


Porosity P
(% lump volume)
$R=\frac{\Delta P}{\Delta \log d}$
WEIGHT % OVERSIZE
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
26
24
22
20
18
16
14
12
10
8
6
4
2
100
90
80
70
60
50
40
30
20
10
1500 1000 500

982759 COMPLETE SPECIFICATION

3 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 1

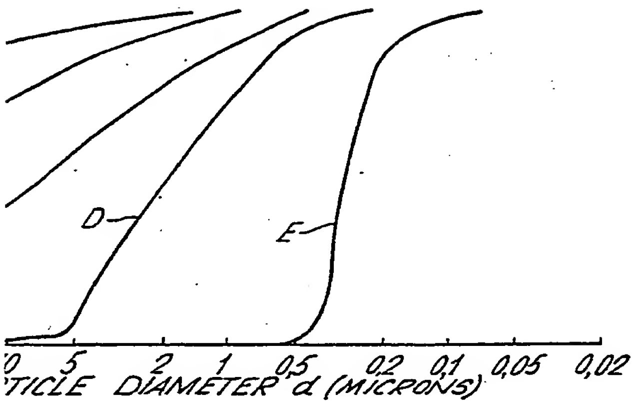


FIG.2.

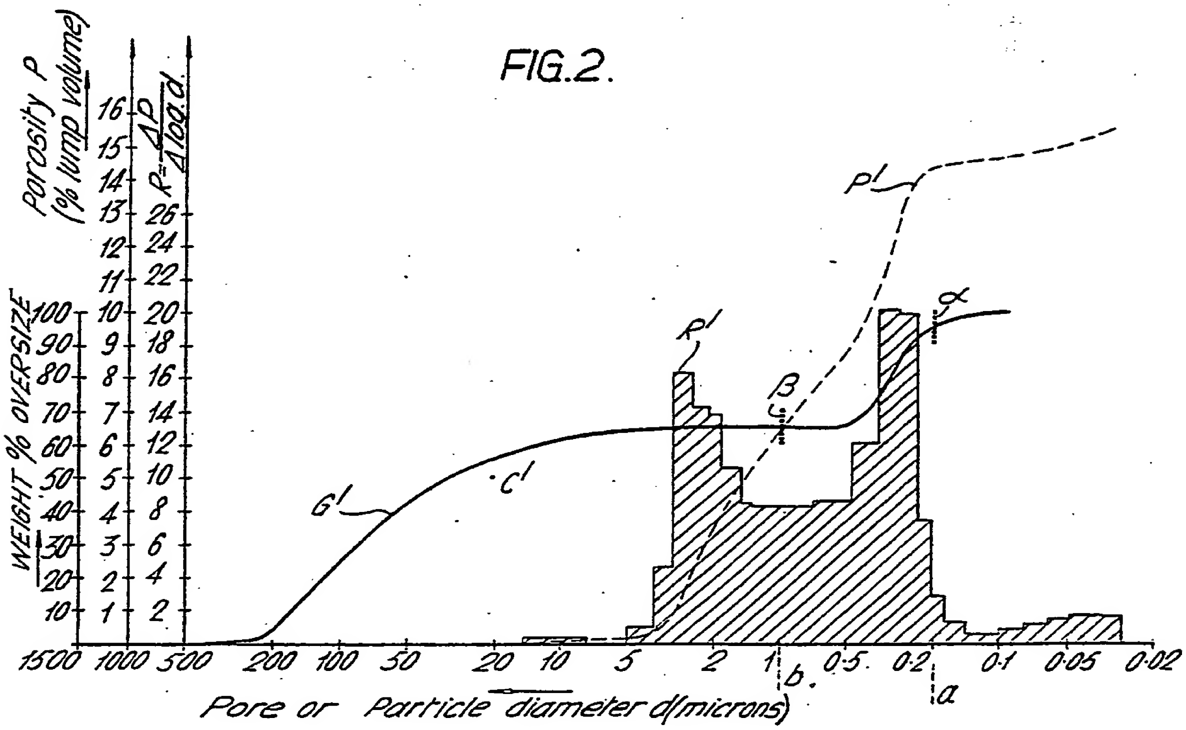
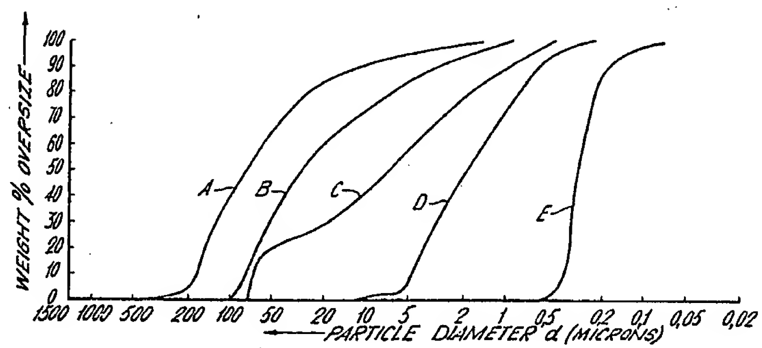


FIG.1.


WEIGHT % OVERSIZE
100
90
80
70
60
50
40
30
20
10
0
A
B
C
D
E
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PARTICLE DIAMETER d (MICRONS)

FIG.2.

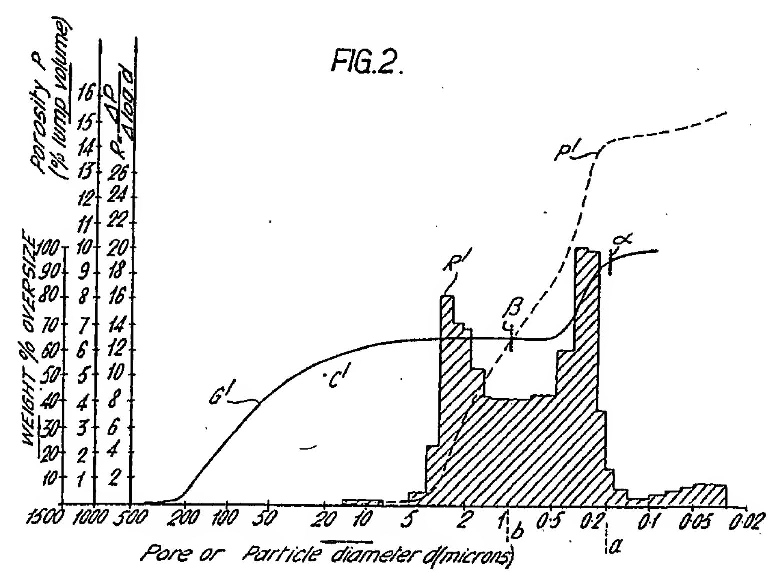
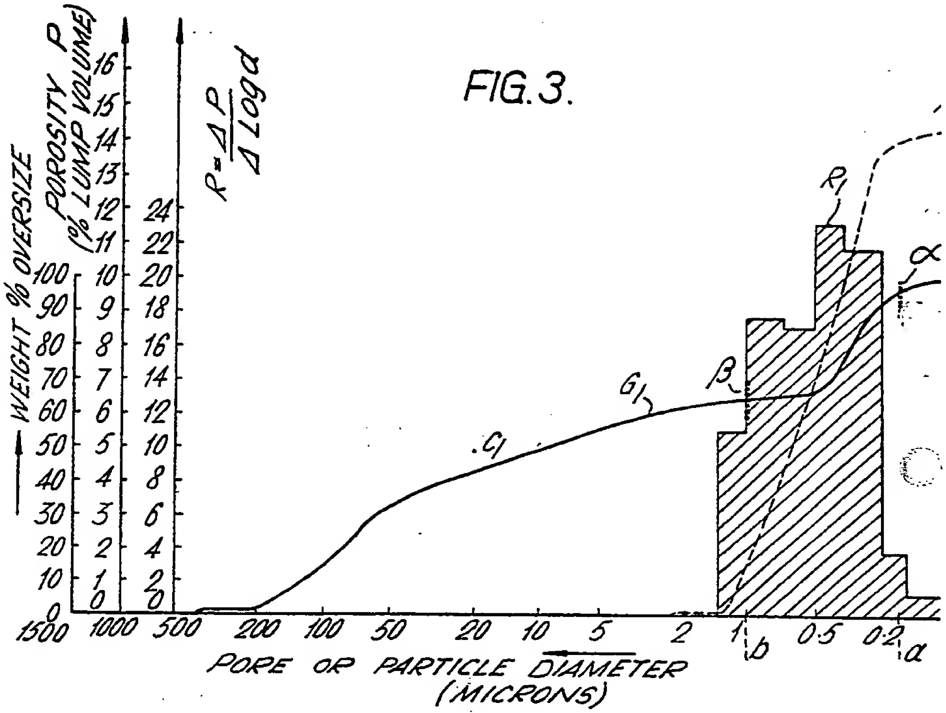
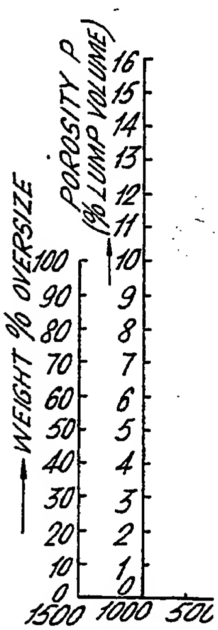

Porosity P (% lump volume)
$R = \frac{\Delta P}{\Delta \log d}$
WEIGHT % OVERSIZE
P'
R'
β
α
G'
C'
1500 1000 500 200 100 50 20 10 5 2 1 0.5 0.2 0.1 0.05 0.02
b
a
Pore or Particle diameter d (microns)

FIG. 3.


WEIGHT % OVERSIZE
POROSITY P
(% LUMP VOLUME)
$R = \frac{\Delta P}{\Delta \log d}$
R_1
G_1
C_1
α
β
a
b
PORE OR PARTICLE DIAMETER
(MICRONS)


WEIGHT % OVERSIZE
POROSITY P
(% LUMP VOLUME)

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3 SHEETS *This drawing is a reproduction of the Original on a reduced scale*
Sheet 2

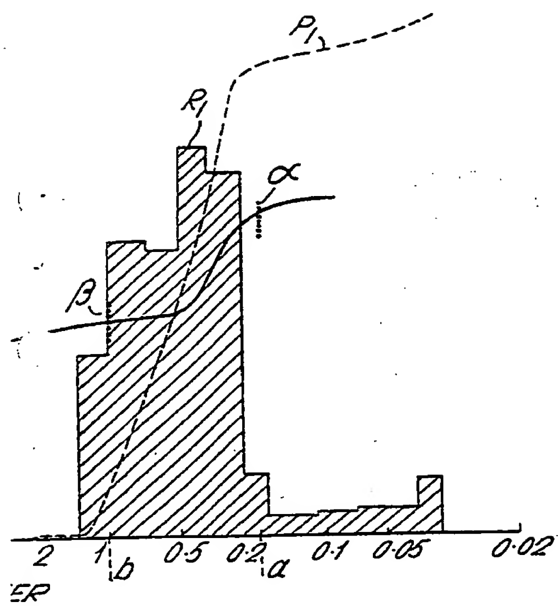


FIG.4.

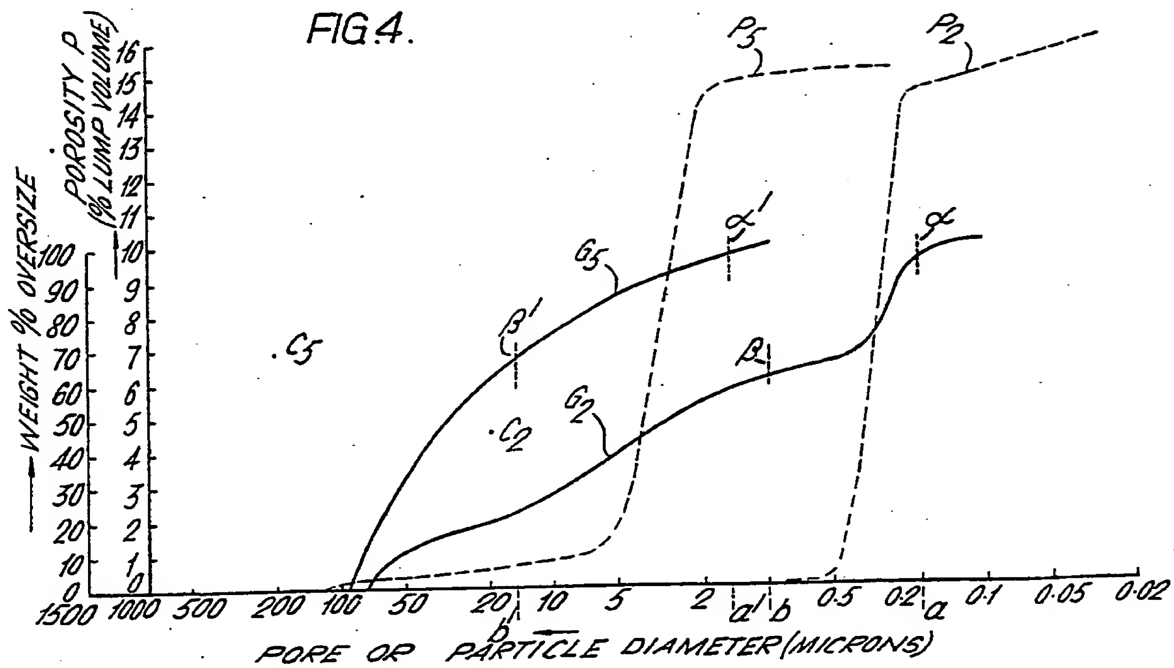


FIG.3.

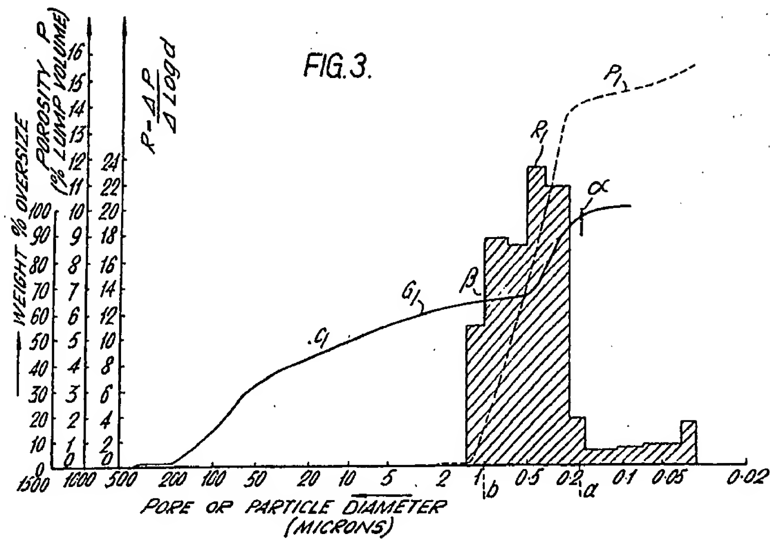

WEIGHT % OVERSIZE
POROSITY P (% LUMP VOLUME)
$R=\frac{\Delta P}{\Delta \log d}$
P_1
R_1
α
β
G_1
C_1
PORE OR PARTICLE DIAMETER (MICRONS)

FIG.4.

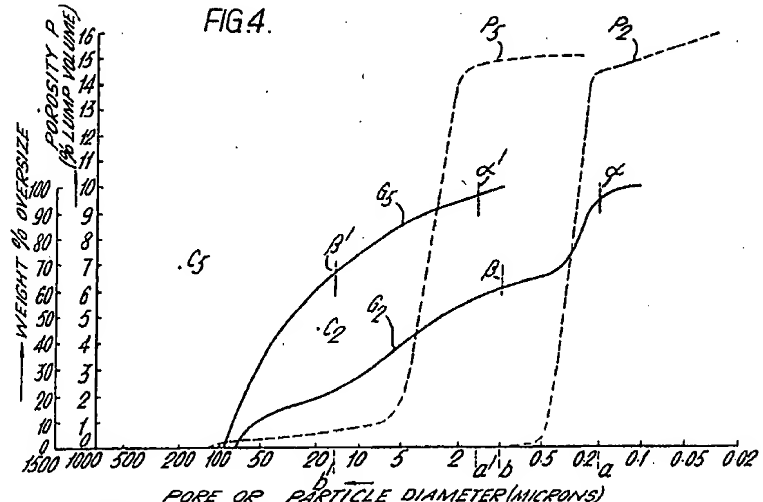
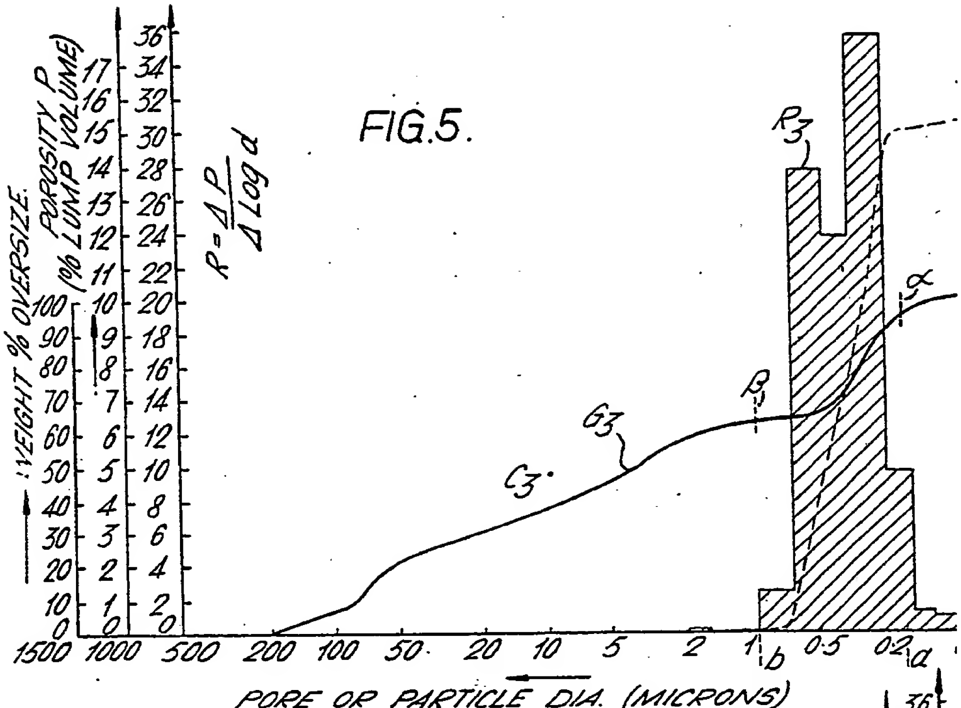
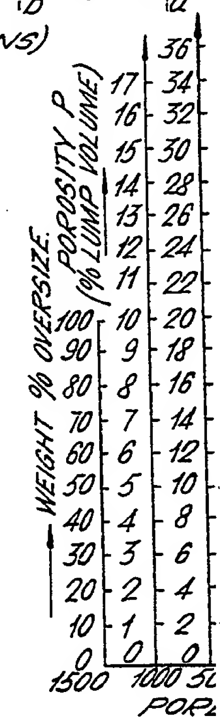

WEIGHT % OVERSIZE
POROSITY P (% LUMP VOLUME)
P_3
P_2
α'
α
G_5
β'
β
C_5
C_2
G_2
PORE OR PARTICLE DIAMETER (MICRONS)

FIG.5.


WEIGHT % OVERSIZE.
POROSITY P
(% LUMP VOLUME)
R = ΔP / Δ Log d
R_3
G_3
C_3
β
α
b
a
1500 1000 500 200 100 50 20 10 5 2 1 0.5 0.2
PORE OR PARTICLE DIA. (MICRONS)


WEIGHT % OVERSIZE.
POROSITY P
(% LUMP VOLUME)
1500 1000

982759 COMPLETE SPECIFICATION
3 SHEETS This drawing is a reproduction of the Original on a reduced scale
Sheet 3

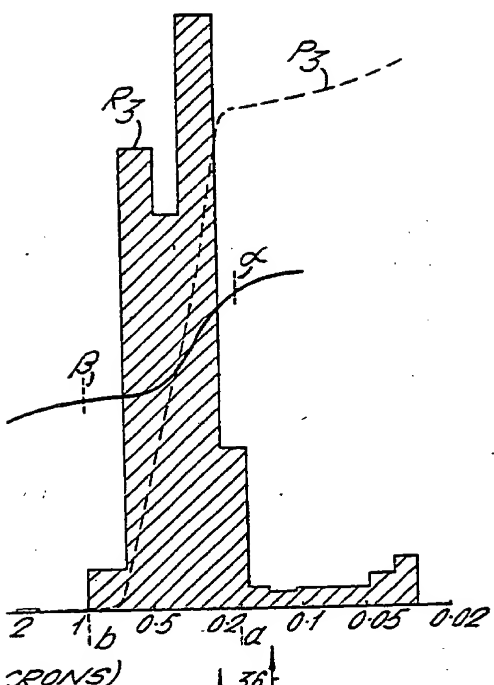
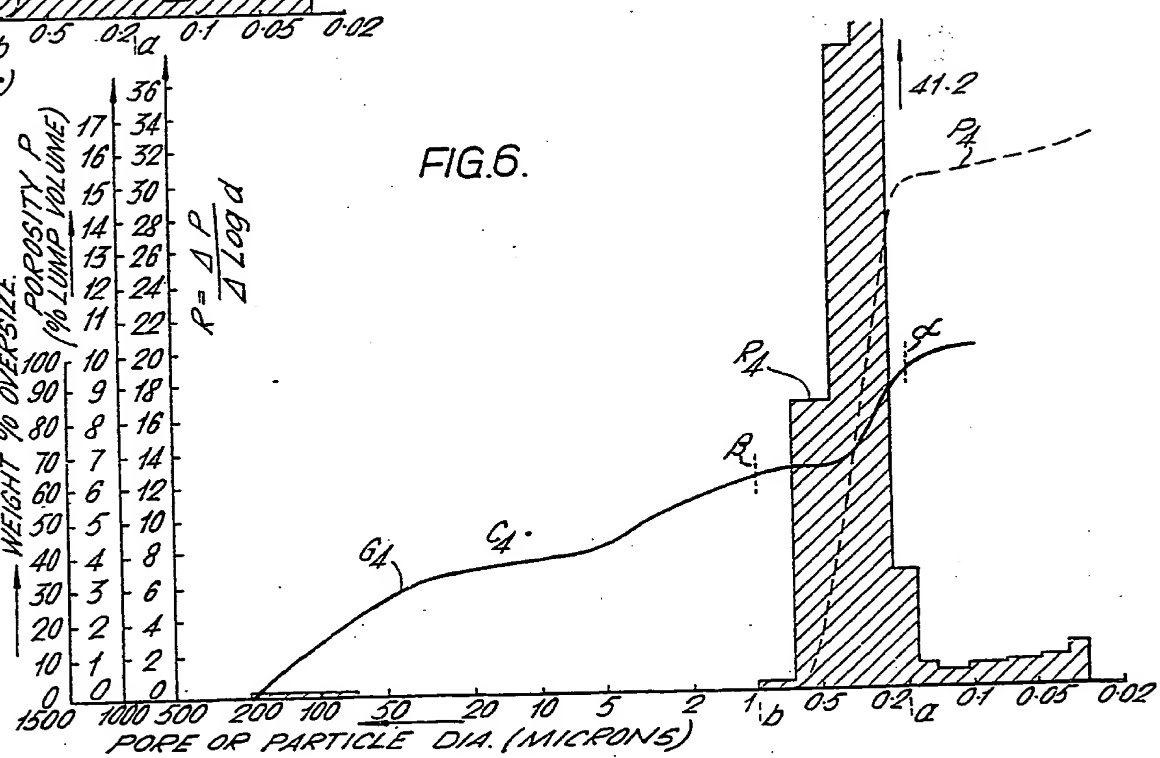


FIG.6.



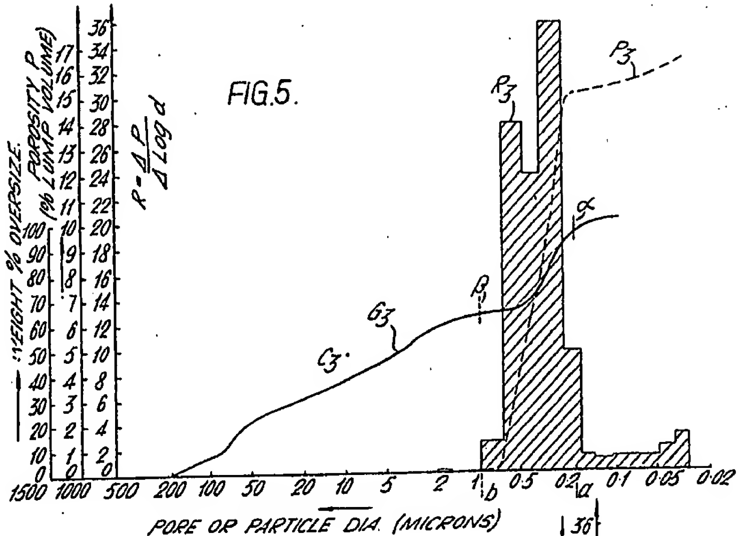

WEIGHT % OVERSIZE
POROSITY P (% LUMP VOLUME)
$R = \frac{\Delta P}{\Delta \log d}$
P_3
R_3
α
β
G_3
C_3
b
a
1500 1000 500 200 100 50 20 10 5 2 1 0.5 0.2 0.1 0.05 0.02
PORE OR PARTICLE DIA. (MICRONS)

FIG.5.

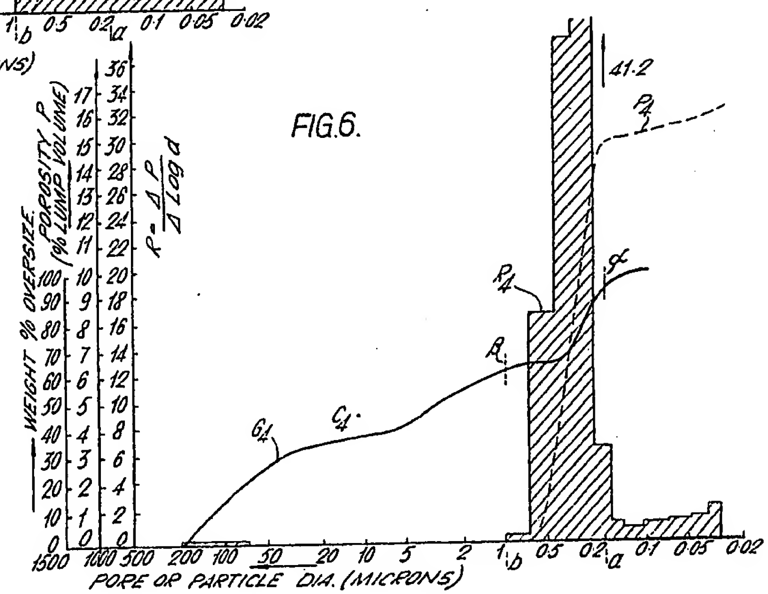

WEIGHT % OVERSIZE
POROSITY P (% LUMP VOLUME)
$R = \frac{\Delta P}{\Delta \log d}$
41.2
P_4
R_4
α
β
G_4
C_4
b
a
1500 1000 500 200 100 50 20 10 5 2 1 0.5 0.2 0.1 0.05 0.02
PORE OR PARTICLE DIA. (MICRONS)

FIG.6.